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(54) **Method by reduction of nitrogen oxide.**

(57) The present invention relates to a method by reduction of nitrogen oxides in gas mixtures, especially removing/decomposition of nitrogen oxide in hot combustion gases. The hot gas mixture which contains N_2O is given a retention time of 0.1-3 seconds before being cooled down. About 90% of N_2O is hereby decomposed to N_2 and O_2. A hot gas mixture formed by catalytic combustion of ammonia is given a retention time of 0.5-2 seconds before it is cooled in a heat recovery unit. The combustion gases can also be brought in contact with a metal or metal oxide catalyst for selective decomposition of N_2O.

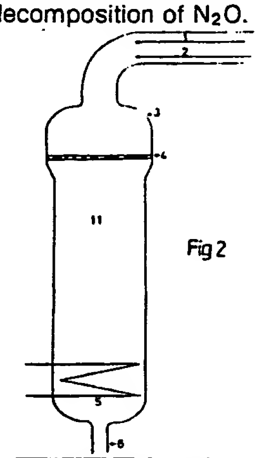

Fig 2

EP 0 359 286 A2

The present invention relates to reduction of dinitrogen oxide which for instance is formed during catalytic combustion of ammonia and oxygen to nitrogen oxides, which thereupon are cooled in a heat recovery unit and then absorbed in water and/or diluted nitric acid.

Nitric acid is manufactured by catalytic combustion of ammonia with oxygen and subsequent absorption of thereby formed nitrogen oxides in water and/or diluted nitric acid. In modern pressure absorption units one has obtained a substantial reduction of the nitrogen oxide (NO_x) emission in the effluent gases. The effluent gas from the most efficient absorption units contains only about 200 ppm NO_x. It is also known to apply catalytic decomposition of nitrogen oxides to nitrogen and water by reacting NO_x with ammonia over a catalyst in order to meet the environmental emission requirements.

During the catalytic combustion of ammonia it is mainly formed NO and NO_2, but 1-2% of the ammonia is converted to dinitrogen oxide (N_2O). Investigations have shown that N_2O does not react or become absorbed in the subsequent process. This implies that all the N_2O formed during the combustion leaves the plant with the effluent gas. Lately one has started to find out whether N_2O in spite of the fact that it is not very reactive, or possibly just because of its long life time in the atmosphere, can represent environmental detrimental effects. Theoretical model tests indicate that N_2O can contribute to the destruction of the ozon layer in the atmosphere.

N_2O, also called laughing gas, is supplied in anesthetic gas in hospitals, and for such small volumes of gases having high concentration of N_2O it is known to decompose N_2O catalytically. It is for instance from Japanese patent application No. 55031463 known to perform such decomposition at 150-550 °C over a platinum catalyst.

It is further reported some theoretical studies in the literature about decomposition of N_2O. Decomposition of N_2O is for instance used as a model reaction for studying catalysts for selective oxidation. These studies are, however, related to small volumes of gas mixtures having high N_2O concentration and not to technical units or nitric acid production and the operating conditions which then must be applied.

W.M. Graven, Journal of American Chemical Soc. 81, 6190 (1959) has reported kinetic studies of homogeneous decomposition of N_2O at 800-1000 °C. In this report it is claimed that the reaction is of first order with regard to N_2O and that NO has a certain accelerating effect and O_2 a retarding effect. It was further observed both decomposition to $N_2 + O_2$ and to NO_2, but the decomposition to $N_2 + O_2$ was dominating. The first order rate constant is stated to be:

$k = 2.1 \cdot 10^9 \exp(-220\,000/RT)\ \text{sec}^{-1}$

R is in Joule/mol °K and

T is in degrees °K

These measurements are, however, carried out in a reaction vessel of 5.6 ml on a N_2O gas diluted with helium. Small amounts of NO and O_2 were added for studying their influence on the N_2O decomposition. At increasing NO concentration it is reported that the reaction $N_2O + NO = NO_2 + N_2$ rapidly became dominating.

It is accordingly no clear guidance to be found in the literature about how one in a technically and economically acceptable way can remove selectively or decompose N_2O from those gas mixtures being present in the nitric acid plant and under those operating conditions which there exist.

The object of the present invention was to remove or decompose a substantial part of the N_2O formed during combustion of ammonia in a nitric acid plant.

A further object was to carry out this decomposition without having to alter substantially the operating conditions during combustion or absorption. It was preferably desired to perform the decomposition at an earliest possible stage in the process.

As mentioned above, it is known several catalysts for decomposition of N_2O, but their selectivity is not known. The most active ones seem to be the nobel metal catalysts which also are applied for combustion of ammonia. These are expensive catalysts and arrangement of such catalysts in the effluent gas from the absorption tower was not considered to be attractive. The reason for this is mainly that there the N_2O concentration is low and also the temperature is relatively low resulting in a correspondingly low rate of conversion. It would also be necessary to use large amounts of catalyst in order to obtain desired decomposition of N_2O with the large volumes in question.

The inventors therefore started their investigation in view of obtaining selective decomposition of N_2O in the combustion unit itself. Commercial ammonia combustion is usually performed at 1125-1229 °K over nobel metal catalysts. The hot reaction gases are then rapidly cooled in a heat recovery unit in the combustion unit right after the catalyst package which usually comprises several nobel metal gauzes and recovery gauzes for nobel metal, first of all platinum.

Based on the indications in the literature that N_2O will decompose relatively rapidly at those operating temperatures present in the combustion unit, it was started investigations in a pilot plant in order to find out

whether the decomposition was selective with regard to N_2O. One would also find out how rapid this decomposition was in the gas having the composition used in a commercial nitric acid plant, especially that gas mixture present just ahead of the heat recovery unit. These investigations were carried out by leading the gas mixture through respectively a steel pipe and a quartz pipe using varying temperatures. It was surprisingly found that in the quartz pipe the rate constant for the decomposition of N_2O was about five times as high as reported in the above referred article. It was further found that contrary to that indicated in this article presence of relatively large amounts of NO was not of substantial influence. The decomposition was very selective with regard to N_2O as registered changes of NO and NO_2 concentration during 1-2 seconds at the actual temperature were almost negligible. It was also carried out experiments with relatively low temperature and it was for instance found that at 960° K the decomposition of N_2O was as low as 1%. The experiments carried out in a steel pipe showed that the decomposition there was far less selective with regard to N_2O as already after 1 second at 1100° K, 7,2% of the $NO + NO_2$ content of the gas was decomposed.

The inventors found that from these investigations and further tests at least 90% of N_2O formed during the combustion could be removed/decomposed selectively in the combustion unit if it was secured that the combustion gases were given sufficient retention time at high temperature, i.e. between the catalyst package and the heat recovery unit. Increased retention time in this area implies that the distance between the catalyst package and the heat recovery unit has to be increased.

In order to reduce the retention time for desired decomposition of N_2O, a metal or metal oxide catalyst which selectively decomposes N_2O after the catalyst package can be installed.

The invention is as defined in the attached patent claims.

The invention will now be further shown and explained in connection with the figures and the examples.

Fig. 1 shows schematically a conventional ammonia combustion unit connected to an absorption tower.

Fig. 2 shows a combustion unit for application of the invention.

Fig. 3 shows a different design of the combustion unit shown in Fig. 2.

Fig. 1 shows schematically a conventional nitric acid unit comprising a combustion unit 3 to which ammonia 1 and oxygen/air 2 are supplied to the upper part of the unit 3.

The gases are converted catalytically in the gauze package 4 and thereupon cooled in the heat recovery unit 5 before they are transported through pipe 6 to an absorption tower 7 in which the nitrogen oxides are absorbed countercurrently. Water is supplied to pipe 8 and product acid removed through pipe 10. The effluent gases containing non-absorbed nitrogen oxides leave the tower through pipe 9.

Fig. 2 shows a combustion unit 3 for carrying out the method according to the invention. The reaction gases leave the unit 3 through pipe 6 to a conventional absorption tower (not shown on the figure). Between the gauze package 4 and the heat exchanger 5 there is arranged an extra volume 11 which results in that the reaction gases get an extra retention time at high temperature, substantially the reaction temperature, before they are cooled down and transported to the absorption tower.

Fig. 3 shows in principle the same type of combustion unit as shown in Fig. 2, i.e. having an exta volume 11. But in order to obtain a low height for the combustion unit it is divided in two and the heat recovery unit 5 is now arranged in a separate unit 12. It is hereby obtained the same retention time for the hot reaction gases as in the unit according to Fig. 2, but the height of the complete combustion unit is substantially lower and that might in several cases be of importance, especially for restructuring of old units.

Example 1

This example shows investigations of the nitrogen oxide decomposition in a gas mixture corresponding to that present right after the catalyst package in an ammonia combustion unit. The tests were carried out at 5 bar in a steel pipe and the gas mixture was given a retention time of 1 second at the actual temperatures. The amounts $NO + NO_2$ and N_2O are stated at the inlet and outlet of the adiabatic reactor (steel pipe). Th remaining gases in the mixture are essentially N_2.

Table 1

Test No	Temp. °K	Vol. % $NO + NO_2$ in	Vol. % $NO + NO_2$ out	% decomp. $NO + NO_2$	ppm N_2O in	ppm N_2O out
1	1100	9.46	9.40	0.6	1700	1030
2	1118	9.51	9.41	1.1	1678	890
3	1141	9.87	9.53	3.4	1495	584
4	1153	10.00	9.48	5.2	1482	464
5	1161	10.10	9.37	7.2	1303	353

Decomposition of $NO + NO_2$ during the tests in the steel pipe were that large that further tests in the steel pipe were stopped. It seemed that the steel pipe had a certain catalytic effect with regard to decomposition of NO.

Example 2

This example shows investigations carried out in a quartz pipe on the same type of gas mixture as in Example 1. The tests were carried out with a retention time of respectively 1 and 2 seconds. Decomposition of $NO + NO_2$ was not registered and in the table the amount for these components are therefore given for the inlet gas.

Table 2

Test No	Temp. °K	Vol. % $NO + NO_2$	ppm N_2O in	ppm N_2O out	Retention time seconds
6	1100	9.46	1700	1101	1
7	1118	9.50	1680	893	1
8a	1141	9.88	1500	558	1
8b	1141	9.88	1511	220	2
9a	1153	10.02	1453	428	1
9b	1153	10.02	1505	135	2
10a	1161	10.01	1389	340	1
10b	1161	10.01	1217	79	2
11a	1175	10.04	1117	170	1
11b	1175	10.04	1109	30	2

As can be seen from Table 2, on obtained selective decomposition of N_2O to N_2 and O_2 and at a temperature corresponding to the actual operating temperature during ammonia combustion, for instance 1175 °K. At a retention time of 1 second about 84,8% was decomposed and at a retention time of 2 seconds about 97,3% was decomposed. Based on these investigations one arrived at the following rate constant k for the homogeneous decomposition:

$k = 4.23 \ 10^9 \exp(-210700/RT) \ \mathrm{sec}^{-1}$

R is in Joule/mol °K

T is in degrees °K.

This rate constant was found to be larger and increase stronger with increasing temperature than the theoretical estimates. reported in the literature. The fact that decomposition proved to be very selective and being that rapid makes it practically possible to give the combustion gases an extra retention time sufficient for decomposing about 90% of the N_2O formed during the ammonia combustion. This implies in practice that in a burner unit an extra volume 11 can be arranged as shown in Figs. 1 and 2.

Further investigations showed that at 1063 °K about 30% of the N_2O was decomposed already after 0.2 seconds and it was found that substantial amounts of N_2O in the warm effluent gases could be removed by

giving them a retention time of 0.1-3 seconds. For decomposition of N_2O in the ammonia combustion unit it should be applied a retention time of 0.5-2 seconds at the existing temperatures.

One has by the present invention been able to remove substantially all of the N_2O formed in connection with nitric acid production. This decomposition of N_2O can be carried out without reduction of the ammonia combustion yield or the efficiency of the nitric acid plant. The method according to the invention can also be carried out without altering the operating conditions for th ammonia combustion or the absorption of nitrogen oxides. The invention can further be applied on other warm gas mixtures from which it is desired to remove N_2O.

Claims

1. Method by reduction of dinitrogen oxide which for instance is formed during catalytic combustion of ammonia and oxygen to nitrogen oxides and thereupon cooled in a heat recovery unit and then absorbed in water and/or diluted nitric acid,
characterized in that
the warm combustion gases are given a retention time of 0.1-3 seconds before they are cooled.

2. Method according to claim 1,
characterized in that
the hot gas mixture formed during the catalytic combustion of ammonia is given a retention time of 0.5-2 seconds before they are cooled in a heat recovery unit.

3 Method according to claim 1,
characterized in that
the combustion gases are brought in contact with a metal or metal oxide catalyst for selective decomposition of N_2O.

4 Method according to claim 1,
characterized in that
the gases leaving the absorption unit are brought in contact with a metal or metal oxide catalyst for decomposition of N_2O.

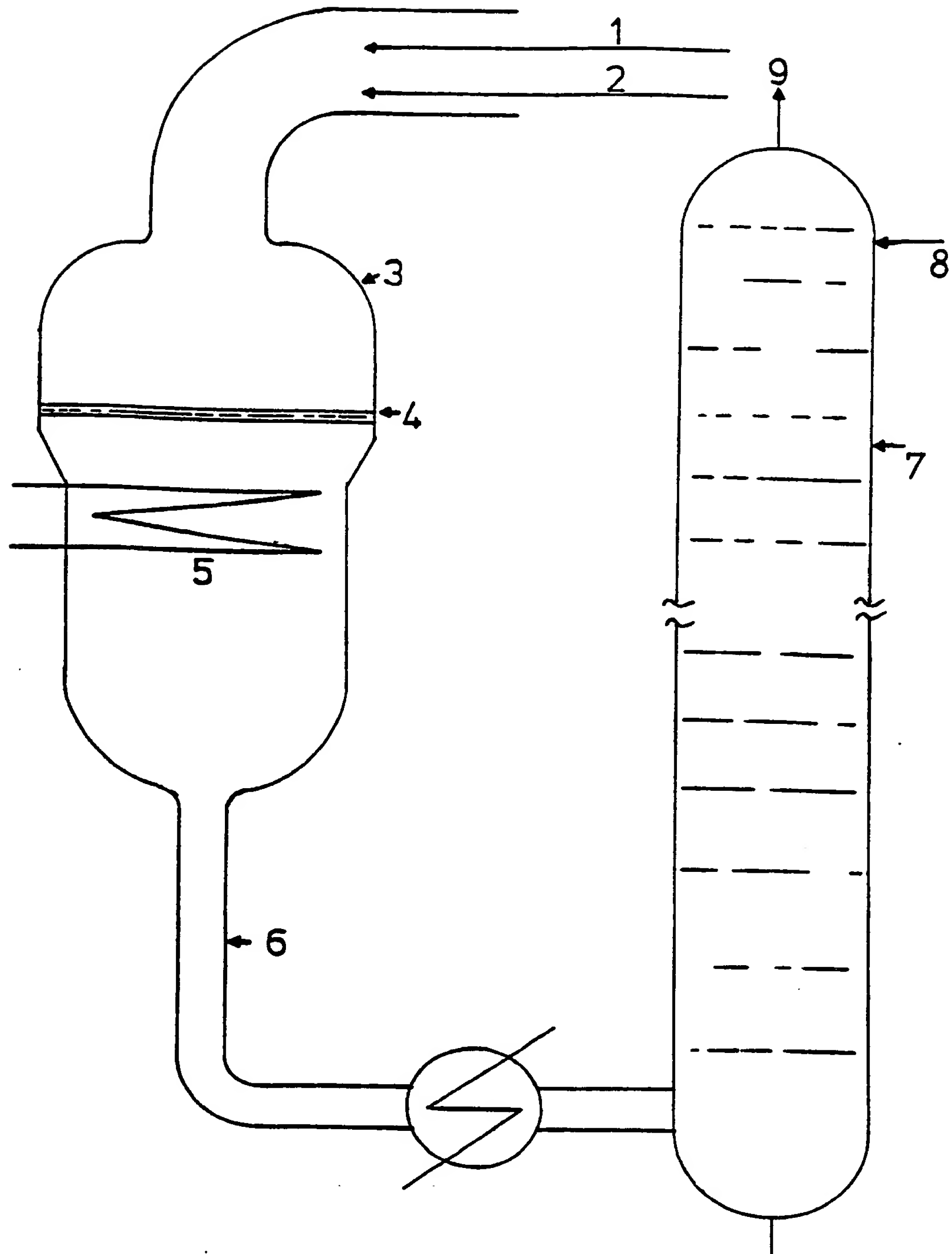

Fig 1

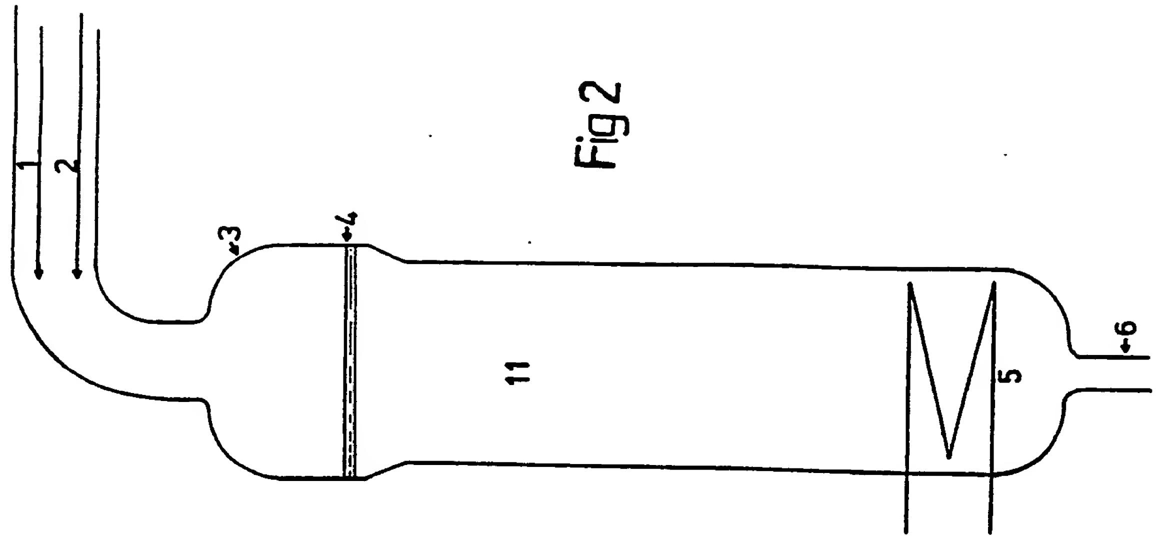

Fig 2

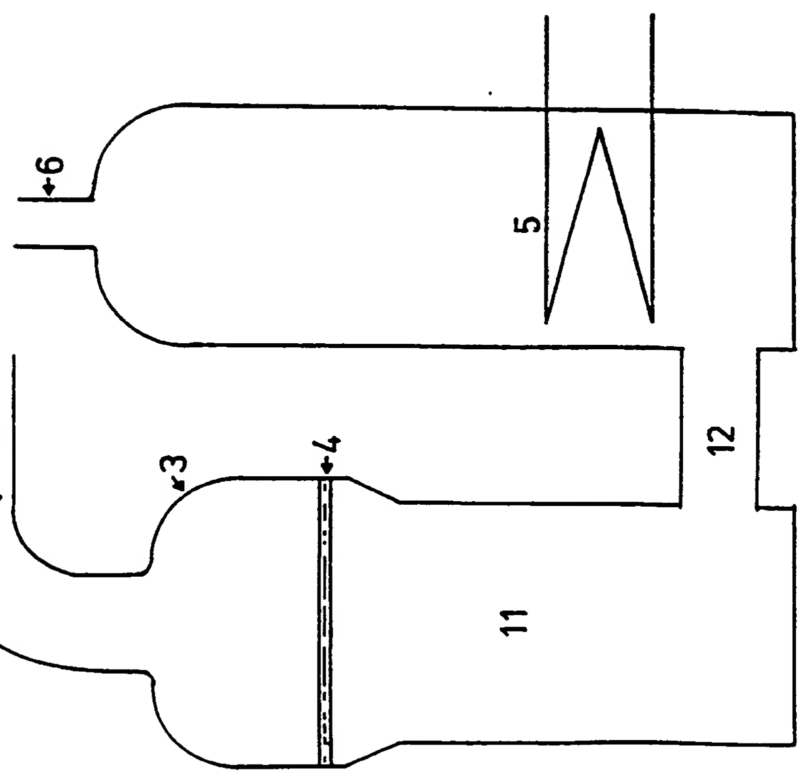

Fig 3

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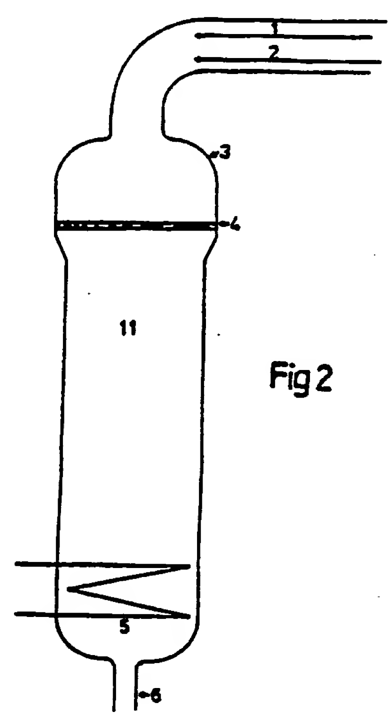

Fig 2

EP 0 359 286 A3

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EUROPEAN SEARCH REPORT

Application Number

EP 89 11 7143

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-A-2601077 (MITSUBISHI CHEMICAL IND.) * claims 1-3 * ---	1-3	B01D53/34
A	US-A-4562052 (G.D.GRAB ET AL.) * column 2, lines 25 - 46 * ---	1	
A,D	PATENT ABSTRACTS OF JAPAN vol. 4, no. 65 (C-10)(547) 16 May 1980, & JP-A-55 31463 (KURARAY K.K.) 05 March 1980, * the whole document * ---	1, 3	
A	CHEMICAL ABSTRACTS, vol. 85, 1976 Columbus, Ohio, USA R. SCHLEPPY et al.: "Reduction of nitric oxide on fiber glass" page 286; ref. no. 85:197349E &Ind.Eng.Chem., Prod.Res.Dev.,Vol,15,No3,1976, pages 172-176 * abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			B01D C01B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	26 NOVEMBER 1990	BERTRAM H.E.H.

CATEGORY OF CITED DOCUMENTS

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